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# Semi-Empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils

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# SEMI-EMPIRICAL ESTIMATION OF SORPTION OF HYDROPHOBIC POLLUTANTS ON NATURAL SEDIMENTS AND SOILS

Samuel W. Karickhoff

Environmental Research Laboratory
U.S. Environmental Protection Agency
Athens, GA 30613

ABSTRACT -- Methods were developed for estimating the equilibrium sorption behavior of hydrophobic pollutants. At low pollutant concentration (aqueous phase concentration less than half the solubility), sorption isotherms were linear, reversible, and characterized by a partition coefficient, $K_p$. Partition coefficients normalized to organic carbon, $K_{OC}$ ($K_{OC} = K_p$/fraction organic carbon), were highly invariant over a set of sediments and soils collected from throughout the nation. Equations for estimating $K_{OC}$ from water solubility (including crystal energy) and octanol/water partition coefficients were developed. The predictive equations were tested on literature sorption data and found to estimate measured $K_{OC}$'s generally within a factor of two.

## INTRODUCTION

Predicting the transport, transformation, or potential biological effects of a toxic chemical in aquatic systems requires knowledge of the physical disposition of the chemical between the sorbed and solution phases. In considering sorption to natural sediments, the high degree of variability and complexity in sediment composition and large number of potential sorptive interactions would seem to preclude the possibility of developing a simple, systematic procedure for predicting sorption parameters. The key to development of such a predictive technique is justifiable simplification - justifiable in that physical rationale or basis, combined with considerable phenomenological evidence or supportive data, can be obtained; simplified not only in the selection of mathematical format but in the amount of system characterization required in its usage. If one treated, in toto, all aspects of this complex problem, hopeless complication would likely arise, and in the end, confusion in lieu of understanding and utility would result.

Recently, researchers have become increasing aware of the importance of sorption phenomena in the fate of aquatic toxicants, although sorption to natural sorbents is certainly not a new area. The agronomy literature over the past 20 years contains numerous studies of sorption in ag-chemical/soil systems. These studies focused primarily on the role of sorption in pesticide activity in soils. More recent studies, however, address pesticides as environmental pollutants and the contributory role of sorption. These pesticide/soil studies have provided some key concepts that form the basis of the present work; however, the actual data are typically of limited value for the development of a generalized predictive scheme for aquatic systems because the pesticide concentrations were often much higher than levels normally found in aquatic systems. Often concentrations were chosen either to approximate field conditions at the time of pesticide application or to meet analytical detection requirements. Moreover, the span of pesticide concentration in a given isotherm was generally less than an order of magnitude. Another characteristic of most pesticide/soil sorption studies is the use of the curvilinear Freundlich equation to describe the sorption behavior. This equation is strictly empirical and, for our purposes, suffers from a lack of physical rationale for extrapolation of specific sorption measurements either out of the range (pesticide concentration) of measurement, or to other sorbent systems. These factors, no doubt, have contributed much complexity and confusion for those in search of congruity in the numerous published pesticide/soil sorption studies.

As early as 1962, however, Goring (1) demonstrated the significance of organic carbon in controlling the sorption of neutral pesticides to soils. This organic carbon-referenced

sorption approach was further developed by Goring (2), Hamaker and Thompson (3), and Lambert (4,5). In addition, Lambert equated the role of soil organic carbon in sorption to that of a water-immiscible organic solvent in solvent extraction and suggested the correlation between sorption coefficients and solvent/water distribution coefficients. Briggs (6) showed such a correlation for the soil sorption of phenyl urea herbicides and their respective octanol/water distribution coefficients.

The present work builds on these key findings in pesticide/soil systems and describes the sorption of hydrophobic pollutants on natural sediment; special emphasis is placed on simple descriptors that provide for:

(1) a priori estimation of equilibrium sorption behavior
(2) extrapolation of sorption measurements in given sediment/sorbate systems to other sediments or other structurally similar sorbates
(3) evaluation or screening of existing sorption data based on "expected behavior"
(4) establishment of relationships (including thermodynamic rationale) of sorption parameters to other physical properties of the sorbate.

## EQUILIBRIUM SORPTION - PARTITION COEFFICIENT

Equilibrium sorption is described graphically by a sorption isotherm, which is a plot of pollutant concentration in the sorbed phase (denoted S) versus pollutant concentration in solution (C). Sorption isotherms are typically measured at constant temperature and at constant sorbent concentration.

Thermodynamically, sorption equilibrium can be defined as the state at which the pollutant fugacities in the sorbed and solution phases are equal.

$$f^S = f^W \tag{1}$$

where the superscripts s and w refer to the sorbed and solution phases, respectively. [Mackay (7) has recently described the use of fugacity in environmental systems.]

Moreover, even if the sorbent, such as a sediment, is pictured as a composite mixture of different sorbents (each indicative of some significant change in sorption mechanism or sorption environment), the fugacity within each sorptive compartment must be equal at equilibrium.

$$f_i^S = f^W \quad \text{for all sorptive compartments (i).}$$

The fugacity or "escaping tendency" can be related to pollutant concentration in each phase. For example, for the aqueous phase,

$$f^W = \phi^W C \tag{2}$$

The fugacity coefficient ($\phi^W$, $\phi^S$, $\phi_i^S$) is commonly expressed as the product of an activity coefficient ($\gamma$) and the corresponding reference state fugacity ($f_o$). This fugacity coefficient is the reciprocal of the fugacity capacity used by Mackay (7). For example,

$$\phi^W = \gamma^W f_o^W \tag{3}$$

The numerical evaluation of any given coefficient ($\phi$) requires the specification of the standard or reference state and its associated fugacity. Also, strictly speaking, concentrations must be in mole fraction units. For low concentrations, however, more conventional units can be used; unit conversion factors are incorporated into the fugacity coefficient, but are only required for numerical evaluation of the individual coefficients.

For the sorbent "mixture," the sorbed pollutant concentration can be taken as a weight-averaged sum of the components.

$$S = \sum_i Y_i S_i = f^S \sum_i \frac{Y_i}{\phi_i^S} \tag{4}$$

where $Y_i$ denote component weight fractions.

The sorbed and solution pollutant concentrations are related by

$$S = C \frac{\phi^W}{\phi^S} \tag{5}$$

In general, fugacity coefficients are dependent upon pollutant concentration and, therefore, the corresponding sorption isotherms are nonlinear. In sufficiently dilute systems, however, these coefficients approach limiting values and the isotherms approach linearity. In simplistic terms, this is the limit in which solute-solute interactions can be ignored in each phase; the molecular environment of the pollutant within each phase remains relatively constant with changes in solute concentration. It is this "lowloading" limit that should be quite typical of most environmental situations,

$$S = K_p C \tag{6}$$

where

$$K_p = \frac{\phi^W}{\phi^S} \quad \text{or} \quad K_p = \phi^W \sum_i \frac{Y_i}{\phi_i^S} \quad \text{for composite sorbents.} \tag{7}$$

$K_p$ is the sorption partition coefficient, and the fugacity coefficients are low-concentration limiting values.

How dilute the system must be to show this limiting behavior varies from system to system depending upon the nature of the solute and type of sorption interaction. Just as in gas-liquid equilibria, where rough rules for adherence to Henry's law can be formulated in terms of solute solubilities and partial pressures (8), a previous study (9) with hydrophobic organics determined that if the equilibrium aqueous phase pollutant concentration is kept below $10^{-5}$ M or below one half of the solute water solubility (whichever is lower), sorption isotherms to natural sediments were linear. More recent works (10-12) substantiate this isotherm linearity for neutral organics. One potentially important source of isotherm nonlinearity is solute speciation changes (aggregation, proton gain or loss, chemical complexation or degradation) not explicity accounted for or experimentally measured or controlled.

The application of the linear sorption model is an important key to the development of estimation and extrapolation methods for all sorption parameters. As discussed previously, the fact that this simple model indeed provides a reasonable representation of real-world sorption in aquatic systems is not simply fortuitous. It is the expected low-concentration behavior and seems to describe sorption at pollutant concentration levels typical of aquatic systems.

## PARTITION COEFFICIENT: DEPENDENCE ON SOIL AND SEDIMENT PROPERTIES

As discussed previously, the relative importance of organic carbon content of a soil or sediment in the sorption of neutral organic pollutants has been well documented. Recently, Kenaga and Goring (13) described the historical development of organic carbon-referenced sorption and gave a rather complete literature listing of studies addressing this phenomenon. The linear dependence of partition coefficient on organic carbon suggests that the partition coefficient factoring for a composite sorbent (eq. 7) can be expressed more simply as

$$K_p \simeq \phi^W \frac{oc}{\phi^{oc}} \tag{8}$$

where organic matter (expressed as fraction organic carbon, oc) constitutes the dominant sorbing component of the soil or sediment. The ratio of fugacity coefficients is usually defined as $K_{oc}$.

$$K_{oc} \equiv \frac{\phi^W}{\phi^{oc}} \tag{9}$$

Furthermore, if the $K_{OC}$ is highly soil or sediment independent, each of the fugacity coefficients, $\phi^{W}$ and $\phi^{OC}$, should be relatively sediment (soil) independent, barring "accidental" cancellation of variations in each. This derives from the dissimilarity of solute environment in the aqueous and sorbent organic phases and corresponding differences in solute interactions with each phase.

Constancy of $\phi^{W}$ implies that the solute activity coefficient in the aqueous phase is relatively insensitive to the inorganic ion and humic acid moieties present in the water, because these would be highly variable in type and degree across a broad range of sediments and/or soils. Consequently, the aqueous phase fugacity coefficient provides a key link in relating $K_{OC}$ to other physical properties of hydrophobic solutes that are not sediment associated. Constancy of $\phi^{OC}$ is also very informative. This indicates a very non-specific sorbate-sorbent interaction, that is, free of site specific bonding which may involve pollutant absorption into organic components. From this stems the analogy, advanced by Lambert, comparing the binding of organic solutes by soil organic components to solute extraction by a water-immiscible solvent. The sorbate binding mechanism would be similar to solvation by an organic solvent, involving predominantly Van der Waals' interactions.

Recently, a set of sediments and soils was collected from throughout the nation by Hassett and Banwart at the University of Illinois on which this $K_{OC}$ variablity was examined for sediments as well as soils. In addition to giving a broad range of natural sources of organic carbon, these sediments/soils provide for the statistical isolation of the organic carbon dependence of sorption from other sorbent properties that are often highly correlated with organic carbon, such as clay mineral content and cation exchange capacity (CEC). Table I gives a brief description of these samples; for a more complete characterization and a correlational analysis of their physical properties, see Hassett et al. (12). This set of sorbents was combined with local (North Georgia) sediments to examine the sediment/soil dependence of $K_{OC}$ for a series of polycyclic aromatic hydrocarbons. Sorption measurements were by conventional batch techniques as described previously for these compounds by Karickhoff et al. (9). Figure 1 shows the variation in $K_p$ with organic carbon for phenanthrene and pyrene. In each case, a 20 to 30-fold variation in $K_p$ was reduced to less than a two-fold variation in $K_{OC}$ by referencing sorption to organic carbon. In addition, at very low carbon contents, an inorganic sorption contribution is contraindicated by the zero intercept. Similar behavior was observed for benzene, naphthalene, and anthracene. Table II shows the mean $K_{OC}$'s for these hydrocarbons on this set of sediments/soils. Correlation coefficients (r) of $K_p$ with organic carbon exceeded 0.90 in all cases.

Hassett et al. (12) found similar behavior on their sediments and soils for additional aromatic hydrocarbons and heterocyclic organics. From these findings, combined with previous pesticide/soil studies recently summarized by Kenega and Goring (13), Rao et al. (14), and Farmer (15), it can safely be generalized that, for neutral organic compounds of limited solubility ($<10^{-3}$M) that are not susceptible to speciation changes or other special complex formation in the sediment/soil suspensions of interest, sorption is "controlled" by organic carbon and is amenable to the $K_{OC}$ format of quantification.

In addition to the primary effect of organic carbon, sediment particle size has been identified as a secondary factor in the sorption of hydrophobic chemicals on natural sediments (9). The primary particle size effect was a reduction of $K_{OC}$ (2 to 10 fold) for sand-sized particles (> 50 μm) relative to $K_{OC}$ for sediment fines (< 50 μm). In practice, however, the majority of the organic carbon is in the fines fraction. The fine material dominates sorption; the sand acts primarily as a diluent. The $K_{OC}$ for the whole sediment approximates that of the fines fraction.

Because the particle size correction is necessary only for "high sand" sediments (> 95 sand), the $K_{OC}$'s and oc's used in this paper are whole-sediment values. It can be assumed, however, that these $K_{OC}$'s are largely those of the fines fraction, with some reduction (10 to 40 ) due to particle size effects. The inclusion of the particle-size dependence of $K_{OC}$ requires knowledge of the organic carbon content of particle size isolates, which is seldom available for field soils or sediments.

## ESTIMATION OF $K_{OC}$

The approach used in estimating $K_{OC}$ combines thermodynamic theory and empirical correlation to relate sorption parameters to widely measured and cataloged properties of sorbates and sediments/soils. Theory is used to suggest the mathematical form relating the physical

Table I. Sediments and Soils: Physical Properties

| No. | Location | %o.c. | clay | silt | CEC me/100g |
|---|---|---|---|---|---|
| 4 | Missouri R., Stanton, ND | 2.07 | 55.2 | 41.8 | 23.7 |
| 5 | Missouri R., Lake Oahe, ND | 2.28 | 31.0 | 35.4 | 19.0 |
| 6 | Missouri R., Big Bend Lake, SD | 0.72 | 68.6 | 31.2 | 33.0 |
| 8 | Missouri R., Onawa, IA | 0.15 | 6.8 | 10.7 | 3.7 |
| 9 | Loess sample, Turin, IA | 0.11 | 17.4 | 75.6 | 12.4 |
| 14 | Soil eroded hillside, Ceredo, WV | 0.48 | 63.6 | 34.4 | 18.9 |
| 15 | Ohio R., Leavenworth, IN | 0.95 | 35.7 | 48.7 | 11.3 |
| 18 | Mississippi R., Columbus, KY | 0.66 | 39.5 | 25.8 | 15.4 |
| 20 | Soil, Fern Clyffe State Park, IL | 1.30 | 28.6 | 71.4 | 8.5 |
| 21 | Illinois R., Lorenzo, IL | 1.88 | 7.1 | 42.7 | 8.3 |
| 22 | Illinois R., Lacon, IL | 1.67 | 21.2 | 52.7 | 8.5 |
| 23 | Confluence of Illinois R. and Sangamon R. | 2.38 | 69.1 | 13.6 | 31.2 |
| 26 | Mississippi R., McClure IL | 1.48 | 42.9 | 55.4 | 20.9 |
| B-2 | Small stream, Watkinsville, GA | 1.21 | 18.6 | 13.9 | 3.7 |
| O.R. | Oconee R., Athens, GA | 0.90 | 5 | 7 | 1.2 |
| D.R. | Doe Run Pond, Athens, GA | 1.30 | 2 | 46 | 2.4 |
| H.H. | Hickory Hill Pond, Athens, GA | 1.40 | 1 | 51 | 2.7 |

Note: Samples 4-26 collected and characterized by John Hassett and Wayne Banwart. B-2 - collected by local EPA personnel and characterized by Hassett and Banwart. O.R., D.R., H.H. - Collected and characterized by local EPA personnel.

Table II. Physical Properties of Polycyclic Hydrocarbons

| | mp | Solubility (ppm) | $K_{ow}$ | $K_{oc}$ | (r)[a] |
|---|---|---|---|---|---|
| Benzene | — | 1790 | 130 | 60 | (0.92) |
| Naphthalene | 80 | 31.7 | 2300 | 870 | (0.93) |
| Phenanthrene | 101 | 1.29 | 37000 | 12000 | (0.96) |
| Anthracene | 216 | 0.073 | 35000 | 16000 | (0.90) |
| Pyrene | 156 | 0.135 | 150000 | 67000 | (0.92) |

[a]Correlation coefficient of $K_p$ versus oc for Table I sediments/soils.

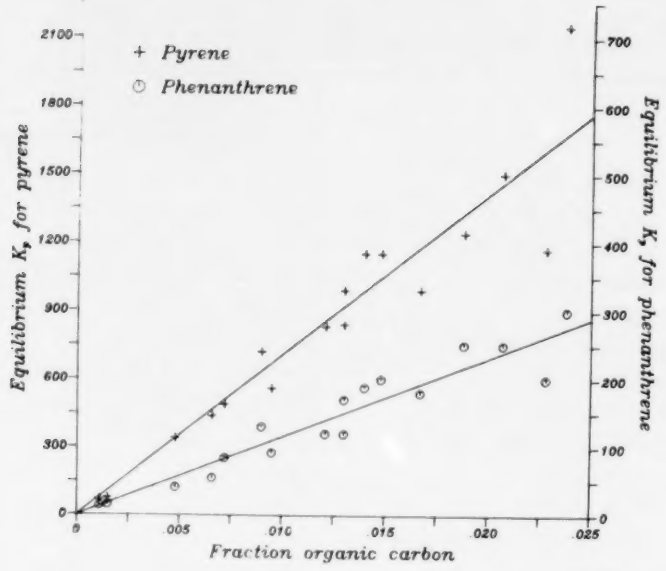


Figure 1. Dependence of Sorption $K_p$ on Organic Carbon for Pyrene and Phenanthrene.

properties, and experimental data are used to empirically establish constants in the mathematical equations. This approach is far preferable to complete reliance on empirical correlation, which cannot be extrapolated out of the narrow range of substances or systems properties on which it is based.

As developed in previous sections, $K_p$ estimation for hydrophobic organics can be reduced to estimation of $K_{OC}$, which, when combined with organic carbon content of the soil or sediment, can yield a good estimate of the sediment-water partition coefficient ($K_p$) (eq. 8). The $K_{OC}$ can be expressed as the ratio of solute fugacity coefficients in the aqueous, $\phi^W$, and organic matter, $\phi^{OC}$, phases (eq. 9). In comparing $K_{OC}$ for a series of hydrophobic solutes on a given soil or sediment, one would expect variations in $K_{OC}$ to be dominated by variations in the aqueous phase coefficient. The large variation in $\phi^W$ derives from the solute-solvent dissimilarity and can be related to solute solubility in the aqueous phase. For example, for the polycyclic organics in Table II, one would expect a 3 to 4 order of magnitude increase in $\gamma^W$ in going from benzene to pyrene. On the other hand, for hydrophobic solutes in association with sediment or soil organic carbon, one would expect solute-sorbent adhesive interactions to be quite similar to solute-solute cohesive interactions with a much smaller range of variability from solute to solute. For a series of hydrophobic solutes, one would expect eq. 9 to reduce to

$$K_{OC} \quad \alpha \quad \gamma^W \tag{10}$$

where the reference fugacity state for the solute is taken to be the pure super-cooled liquid. Because activity coefficients are not commonly used or known, however, $\gamma^W$ is expressed in terms of more readily available physical properties.

$K_{OC}$ from Water Solubility. For hydrophobic liquids, $\gamma^W$ is equal to the reciprocal of the mole fraction solubility, $X_{sol}$. For solutes that are solids at room temperature, a crystal energy term must be added (8,16,17). That is,

$$\log K_{OC} = -\alpha \log X_{sol} + \text{"crystal energy term"} + \beta \tag{11}$$

where $\beta$ depends upon the fugacity coefficient, $\phi^{OC}$; ideally, if $\phi^{OC}$ is relatively independent of solute, $\alpha$ approximates unity.

Commonly, the linear regression of log $K_{OC}$ versus log $X_{sol}$ has been used with no explicit crystal energy contribution (9,10,12,13). For the hydrocarbons in Table II, this linear regression gives:

$$\log K_{oc} = -0.594 \log X_{sol} - 0.197 \qquad (r^2 = 0.945) \tag{12}$$

Although this works well in many instances, the need for including the "crystal energy" contribution in $K_{OC}$ estimation is often apparent if one examines the sorption behavior of structural isomers. For example the $K_{OC}$s for phenanthrene and anthracene differ by only a few percent, as opposed to a nearly 20-fold difference in solubilities. Wahid and Sethunathan (18) found no appreciable differences in the sorption behavior of the $\alpha$, $\beta$, and $\gamma$ isomers of hexachlorocyclohexane (BHC), whereas their measured solubilities (19) differ by a factor of 37 from greatest to least soluble [see Table III]. For organic solutes this crystal term can be approximated [see Prausnitz (8) for a more complete expression] by:

$$\frac{-\Delta S_f\ (mp-25)}{2.303\ R\ 298}$$

where $\Delta S_f$ is the entropy of fusion, mp is the solute melting point in °C; 25°C (298°K) is taken as the reference temperature.

For solutes that are liquids at 25°C, the melting point is "set" at 25°C and the crystal term vanishes. Yalkowsky and Valvani (17,20) have discussed estimation of $\Delta S_f$ in detail. For "rigid" organic molecules, which are solids at 25°C, $\Delta S_f$ is not highly variable (generally 12 to 15 eu). Rigid molecules would include cyclic aliphatic or aromatic compounds containing less than 5 atoms in a flexible chain. For compounds in Table II, $\Delta S_f = 13 \pm .2$ eu (8), and the crystal energy term is given by -.00953 (mp-25). Linear regression with equation (11) including this crystal energy term gives

$$\log K_{OC} = -0.921 \log X_{sol} - .00953\ (mp-25) - 1.405 \qquad (r^2 = 0.995) \tag{13}$$

This crystal energy term significantly improves the quality of fit to the experimental data. Also, the fitted coefficient for the solubility term much more closely approximates unity, thus supporting the assumed dominance of $\gamma^w$ in $K_{OC}$ variations between solutes. Equation (13) should work well for rigid hydrophobic organic solutes, but for non-rigid-organics, a measurement or estimate of $\Delta S_f$ is required (17,20). Fortunately, non-rigid molecules typically melt at much lower temperatures than rigid molecules of similar molecular weight and are frequently liquids at room temperature; thus, the "crystal term" is either zero or very small in most instances.

$K_{OC}$ from $K_{OW}$. The octanol/water partition coefficient ($K_{OW}$) like $K_{OC}$ is a distribution coefficient of solute monomers between an aqueous phase and a hydrophobic organic phase. Thermodynamically $K_{OW}$ can be expressed as the ratio of fugacity coefficients and activity coefficients (16) if the same standard state is chosen in each phase (i.e., pure supercooled liquid solute).

$$K_{OW} = \frac{C_o}{C_w} = \frac{\phi^w}{\phi^o} = \beta \frac{\gamma^w}{\gamma^o} \tag{14}$$

where o and w denote the octanol and aqueous phases, respectively; $\beta$ is a unit adjustment constant converting $C_o$ and $C_w$ to mole fraction units in each phase. Just as was the case in sediment/water systems, $\gamma^w$ can be considered to be the distilled water activity coefficient, unaffected by the presence of octanol (approximately $10^{-3}$ M at 25°C) in the aqueous phase.

By combining equations 9 and 14, $K_{OC}$ and $K_{OW}$ are related by

$$K_{OC} = \frac{\phi^o}{\phi^{oc}} K_{OW} \tag{15}$$

where the proportionality constant is the ratio of fugacity coefficients for the solute dissolved in octanol (saturated with water) and bound in natural organic matter. For $K_{OC}$

Table III. Comparison of Estimated and Measured $K_{oc}$s

| Compound | Measured data (literature) mp°C | $-\log X_{sol}$ | $\log K_{ow}$ | $\log K_{oc}$ | Estimated $\log K_{oc}$ from $K_{ow}$ | from $X_{sol}$, mp | from $X_{sol}$ |
|---|---|---|---|---|---|---|---|
| Hydrocarbons and Chlorinated Hydrocarbons | | | | | | | |
| 3-methyl cholanthrene | 179 | 9.66 (28,12) | 6.42 (12) | 6.09 (12) | 6.03 | 6.02 | 5.54 |
| dibenz[a,h]anthracene | 269 | 9.79 (12) | 6.50 (12) | 6.22 (12) | 6.11 | 5.30 | 5.62 |
| 7,12-dimethylbenz[a]anthracene | 123 | 8.77 (12) | 5.98 (12) | 5.35 (12) | 5.59 | 5.74 | 5.01 |
| tetracene | 335 | 10.43 (28) | 5.90 (9) | 5.81 (9) | 5.51 | 5.25 | 5.99 |
| 9-methylanthracene | 82 | 7.61 (28) | 5.07 (9) | 4.71 (9) | 4.68 | 5.06 | 4.32 |
| pyrene | 156 | 7.92 (28,12) | 5.18 (9,12) | 4.83 | 4.79 | 4.64 | 4.51 |
| phenanthrene | 101 | 6.89 (28) | 4.57 (9) | 4.08 | 4.18 | 4.22 | 3.90 |
| anthracene | 216 | 8.12 (28) | 4.54 (9) | 4.20 | 4.15 | 4.25 | 4.63 |
| naphthalene | 80 | 5.35 (28) | 3.36 (9) | 2.94 | 2.97 | 3.00 | 2.98 |
| benzene | 25[a] | 3.39 (30) | 2.11 (9) | 1.78 | 1.72 | 1.72 | 1.82 |
| 1,2-dichloroethane | 25[a] | 2.82 (10,27) | 1.45 (27) | 1.51 (10) | 1.06 | 1.19 | 1.48 |
| 1,1,2,2-tetrachloroethane | 25[a] | 3.50 (27) | 2.39 | 1.90 (10) | 2.00 | 1.80 | 1.87 |
| | | 3.46 (13) | | | | | |
| 1,1,1-trichloroethane | 25[a] | 3.74 (27,10) | 2.47 (27) | 2.25 (10) | 2.08 | 2.04 | 2.02 |
| tetrachloroethylene | 25[a] | 4.28 (17) | 2.53 (27) | 2.56 (10) | 2.14 | 2.54 | 2.35 |
| | | 4.66 (10) | | | | 2.89 | 2.57 |
| γ BHC (lindane) | 113 | 6.34 (19) | 3.72 (19) | 3.30[b] | 3.33 | 3.60 | 3.57 |
| α BHC | 160 | 6.90 (19) | 3.81 (19) | 3.30[b] | 3.42 | 3.66 | 3.90 |
| β BHC | 309 | 7.91 (19) | 3.80 (19) | 3.30[b] | 3.41 | 3.17 | 4.50 |
| 1,2-dichlorobenzene | 25[a] | 4.74 (27,10) | 3.39 (27) | 2.54 (10) | 3.00 | 2.96 | 2.62 |
| pp' DDT | 109 | 9.79 (31) | 6.19 (32) | 5.38 (13) | 5.80 | 6.81 | 5.62 |
| methoxychlor | 89 | 8.20 (29) | 5.08 (9) | 4.90 (9) | 4.69 | 5.54 | 4.67 |
| 22',44',66' PCB | 114 | 10.35 (33) | 6.34 (9) | 6.08 (9) | 5.95 | 7.28 | 5.95 |
| 22',44',55' PCB | 103 | 9.30 (34) | 6.72 (36) | 5.62 (35) | 6.43 | 6.42 | 5.33 |
| Chloro-s-triazines | | | | | | | |
| atrazine | 172 | 5.56 (37) | 2.33 (14) | 2.17 (13) | 1.94 | 2.31 | 3.11 |
| | | | 2.71 (11) | 2.21 (14) | 2.42 | | |
| | | | | 2.33 (11) | | | |
| propazine | 213 | 6.17 (38) | 2.94 (11) | 2.20 (13) | 2.55 | 2.49 | 3.47 |
| | | | | 2.19 | | | |
| | | | | 2.56 (11) | | | |
| simazine | 226 | 6.35 (39) | 2.16 (11) | 2.13 (13) | 1.77 | 2.53 | 3.66 |
| | | | | 2.14 (14) | | | |
| | | | | 2.33 (11) | | | |
| trietazine | 103 | 4.89 (38) | 3.35 (11) | 2.74 (11) | 2.96 | 2.36 | 3.25 |

Table III. Comparison of Estimated and Measured $K_{oc}$s. (continued)

| Compound | Measured data (literature) mp°C | -log $X_{sol}$ | log $K_{ow}$ | log $K_{oc}$ | Estimated log $K_{oc}$ from $K_{ow}$ | from $X_{sol}$, mp | from $X_{sol}$ |
|---|---|---|---|---|---|---|---|
| Chloro-s-triazines (continued) | | | | | | | |
| ipazine | 87 | 5.53 (39) | 3.94 (11) | 3.22 (13) | 3.55 | 3.10 | 3.09 |
| | | | | 2.91 (11) | | | |
| cyanazine | 167 | 4.89 (13) | 2.24 (11) | 2.30 | 1.85 | 1.75 | 2.71 |
| | | | | 2.26 (11) | | | |
| Carbamates | | | | | | | |
| carbaryl | 142 | 5.45 (38) | 2.81 (26) | 2.36 (13) | 2.42 | 2.50 | 3.04 |
| carboturan | 151 | 4.47 (13) | 2.07 (26) | 1.46 (14) | 1.68 | 1.51 | 2.46 |
| chlorpropham | 41 | 5.13 (13) | 3.06 (26) | 2.77 (13) | 2.67 | 3.17 | 2.85 |
| | | 5.04 (39) | | | | 3.08 | 2.80 |
| Organophosphates | | | | | | | |
| malathion | 25[a] | 5.10 (38) | 2.89 (36) | 3.25 (14) | 2.50 | 3.29 | 2.83 |
| parathion | 25[a] | 5.81 (38) | 3.81 (36) | 3.68 (13) | 3.42 | 3.95 | 3.25 |
| | | | | 4.03 (14) | | | |
| methylparathion | 36 | 5.41 (38) | 3.32 (26) | 3.71 (14) | 2.93 | 3.47 | 3.02 |
| | | | | 3.99 (13) | | | |
| chlorpyrifos | 42 | 6.99 (40) | 3.31 (26) | 4.13(13) | 2.92 | 4.87 | 3.96 |
| | | | 4.82 (41) | | 4.43 | | |
| | | | 5.11 (36) | | 4.72 | | |
| Phenyl Ureas | | | | | | | |
| diuron | 155 | 5.49 (38) | 1.97 (6) | 2.60 (13) | 1.58 | 2.41 | 3.06 |
| | | | 2.81 ((26) | 2.58 (14) | 2.42 | | |
| fenuron | 128 | 3.37 (38) | 1.00 (6) | 1.43 (13) | 0.61 | 0.72 | 1.80 |
| | | 3.50 (39) | | 1.63 (14) | | 0.84 | 1.86 |
| linuron | 93 | 5.27 (13) | 2.19 (6) | 2.91 (13) | 1.80 | 2.80 | 2.93 |
| | | | | 2.94 (14) | | | |
| monolinuron | 76 | 4.31 (38) | 1.60 (6) | 2.30 (13) | 1.21 | 2.08 | 2.36 |
| | | | | 2.45 (14) | | | |
| monuron | 170 | 4.68 (38) | 1.46 (6) | 2.00 (13) | 1.07 | 1.52 | 2.58 |
| | | | 2.12 (26) | 2.26 (14) | 1.73 | | |
| fluometuron | 164 | 5.16 (13) | 1.34 (6) | 2.24 (13) | 0.95 | 2.02 | 2.87 |
| Miscellaneous compounds | | | | | | | |
| 13Hdibenzo[a,i]carbazole | 220 | 9.15 (12) | 6.40 (12) | 6.02 (12) | 6.01 | 5.16 | 5.24 |
| 2,2' biquinoline | 194 | 7.14 (12) | 4.31 (12) | 4.02 (12) | 3.92 | 3.56 | 4.04 |

Table III. Comparison of Estimated and Measured $K_{oc}$s. (continued)

| Compound | Measured data (literature) mp°C | $-\log X_{sol}$ | $\log K_{ow}$ | $\log K_{oc}$ | Estimated $\log K_{oc}$ from $K_{ow}$ | from $X_{sol}$,mp | from $X_{sol}$ |
|---|---|---|---|---|---|---|---|
| dibenzothiophene | 98 | 6.84 (12) | 4.38 (12) | 4.05 (12) | 3.99 | 4.20 | 3.87 |
| acetophenone | 25[a] | 3.09 (12) | 1.59 (12) | 1.54 (12) | 1.20 | 1.40 | 1.64 |
| terbacil | 176 | 4.23 (38) | 1.89 (14) | 1.71 (13)<br>1.61 (14) | 1.50 | 1.05 | 2.32 |
| bromacil | 158 | 4.25 (39) | 2.02 (26) | 1.86 (13) | 1.63 | 1.34 | 2.33 |

[a]Compounds are liquids at 25°C. [b]Computed from sorption data of Wahid et al. (18).

and $K_{ow}$ to be linearly related, this ratio must be independent of solute. Linear regression of $\log K_{oc}$ and $\log K_{ow}$ for the compounds in Table II gives

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346 \quad (r^2 = 0.997) \qquad (16)$$

The near-unity coefficient for $\log K_{ow}$ substantiates the constancy of the ratio of fugacity coefficients (eq. 15) in the organic phases for this series of compounds. Fitting the linear form (eq. 15) gives

$$K_{oc} = 0.411 K_{ow} \quad (r^2 = 0.994) \qquad (17)$$

A priori $K_{oc}$ Estimation from Molecular Fragments. For computing thermodynamic properties, it has often been found useful to consider a molecule as a collection of molecular fragments, each making a distinct contribution to the thermodynamic property, which is relatively independent of the rest of the molecule. The most common application of this general concept is Linear Free Energy Theory (LFET), which has been frequently applied to solute partitioning between phases [i.e., chromatography (21), octanol/water partitioning (22,23), and even sorption to soils (24,25)]. The philosophy behind the method is that a large number of molecular structures can be generated from a relatively small number of fragments, and thus a larger number of thermodynamic estimates can result from a small number of experimental measurements (fragment constants). The accuracy of the prediction, however, necessarily improves as the specificity of the fragment environment increases, which entails an increase in the number of fragments (or corrective factors) that must be considered. Practicality necessitates a compromise. In any given application, this theory is applied at different levels of sophistication. One user may employ a few fragment constants and generate "first order" estimates whereas another may employ numerous corrections or adjustments reflecting more fragment specificity for a given molecular environment. For multiply substituted compounds, good estimates generally require sophisticated input, either in terms of system specific fragment constants or corrective terms. There are some instances, however, where this approach can permit facile extrapolation of $K_{oc}$ measurements.

Addition of ring fragments. For unsubstituted condensed ring aromatics, such as the compounds in Table II, one can write

$$f^{\alpha}_{C_4H_2} = \log K_{oc} \text{ (naphthalene)} - \log K_{oc} \text{ (benzene)}$$

where $f_{C_\alpha H}$ denotes the ring fragment constant for $\alpha$ condensed ring addition (i.e., fragment attached at $\alpha$ carbons). From the data in Table II, $f^{\alpha}_{C_4H_2}$ is 1.16.

With this fragment constant, one can extrapolate to any α condensed ring system. For 3-ring systems, phenanthrene and anthracene, the computed value is 4.10 whereas the measured log $K_{OC}$'s were 4.08 and 4.20, respectively. For 4 and 5-ring systems, the computed values are 5.26 and 6.42; published measured values are 5.81 (9) for tetracene (4 ring) on a sediment fines fraction and 6.22 (12) for the dibenz[a,h]anthracene (5 ring) on the University of Illinois sediments.

Similarly, fragment constants can be derived for ring addition involving 3 carbon addition (β condensation) and 2 carbon addition (γ condensation), which would enable $K_{OC}$ estimation for most condensed (6 membered ring) aromatic hydrocarbons.

Addition of functional groups. The addition of a functional group (X) (replacing a H atom) to a hydrocarbon matrix (R-H) is a primary application of LFET. In this case

$$\log K_{OC}\ (R\text{-}X) - \log K_{OC}\ (R\text{-}H) = \pi_X^S$$

The substituent constants, $\pi_X^S$, are determined experimentally and are relatively system independent for similar organic molecules. System specificity can be especially large for (1) addition of polar functional groups - $NH_2$ and - OH, (2) addition of electron releasing or withdrawing groups to compounds that can potentially ionize in sediment/water systems, and (3) multiple substitution of functional groups on a hydrocarbon matrix. Although this approach is not easily adaptable to a priori estimation of $K_{OC}$ for most pesticides, it does offer considerable potential for mono and di-substituted compounds. In this respect, tremendous advantage can be derived from the relationship between $K_{OC}$ and $K_{OW}$ described in the previous section (eqs. 15, 17). Because $K_{OC}$ and $K_{OW}$ are linearly related, it can easily be shown that the substituent constants, $\pi_X^S$, for sorption are equal to those for the comparable $K_{OW}$ system, $\pi_X^Q$. This makes possible the utilization of this extrapolation procedure without development of an extensive library of substituent constants, $\pi_X^S$. The comparable $K_{OW}$ constants, $\pi_X^Q$, are readily available (22,23) and are generally applicable excepting those instances described previously. It should be emphasized that this extrapolation does not require a knowledge of $K_{OW}$ for either of the specific compounds R-H or R-X in question.

## COMPARISON OF COMPUTED $K_{OC}$'s WITH LITERATURE MEASURED VALUES

In this section, $K_{OC}$ estimates derived from equations 12, 13, 16, and 17 are compared with literature measurements for additional aromatic compounds, aliphatic and aromatic chlorinated hydrocarbons, and compounds containing a wide variety of polar functional groups. Deviations are examined for specific properties or potential sorptive interactions attributable to functional groups or additions to the hydrocarbon matrix.

The hydrocarbons in Table II were selected as test compounds because (1) they form the hydrocarbon framework for a large percentage of aromatic organics and thus constitute a good basis set from which to extrapolate to other compounds,
(2) they hydrophobically sorb with little potential for sorption involving solute dipoles or H-bonding,
(3) the physical properties used for $K_{OC}$ estimation (i.e., $K_{OW}$, $X_{SOL}$) span a range in excess of three orders of magnitude; in addition, good agreement exists among numerous published measurements of each physical property for each compound.

Two recent reviews (13,14) have summarized $K_{OC}$'s from the pesticide/ soil literature. For many compounds this involved computing $K_{OC}$s from published isotherms or other sorption data. In addition, numerous $K_{OC}$s have recently been published for non-pesticides (9,10,12). Table III contains the available $K_{OC}$ data on those compounds for which water solubilities, melting points, and octanol/water distribution coefficients could also be found; computed $K_{OC}$s (eqs. 12, 13, 17) are tabulated for comparison with the measured values. Compounds for which solute speciation could be expected (such as organic bases with pKa > 3) were excluded. Overall, The agreement between calculated and measured $K_{OC}$s was good, generally agreeing within a factor of 3 (or 0.48 log units). This is comparable to typical deviations in $K_{OC}$s reported for a given compound on widely differing sediments or soils. It is difficult to ascribe, with any degree of certainty, descrepancies inherent in the computations, but the following comments are noteworthy.

Hydrocarbons and chlorinated hydrocarbons. For the hydrocarbons and chlorinated hydrocarbons, all three equations (12, 13, 17) give $K_{OC}$ estimates to within the expected variability limits of the data for most compounds. $K_{OW}$ derived estimates for log $K_{OC}$ deviated from measured values an average of 0.20 log units (absolute value deviation). For only one of the 22 compounds was the deviation greater than 0.48 log units or a factor of 3 in $K_{OC}$.

For $K_{OC}$ derived from $X_{SOL}$ with no crystal energy correction, the average deviation was 0.30 log units. The noteworthy deviant that exceeds expected variations due to sediment source or measurement error is the β isomer of BHC, which melts anomalously high (309°C) for its molecular weight. Inclusion of crystal energy considerably improved this $K_{OC}$ estimate. For the high molecular weight chlorinated compounds (DDT, methoxychlor, hexachlorobiphenyls), however, eq. 13, involving $X_{SOL}$ and mp, considerably overestimated (0.64 - 1.43 log units) measured $K_{OC}$'s. This indicates, perhaps, that the assumed constancy of $\phi^{OC}$ breaks down for these compounds, whereas the ratio $\phi^{O}/\phi^{OC}$ (involved in $K_{OC}$ estimation from $K_{OW}$) remains constant. It should be emphasized, however, that for these high molecular weight compounds, large errors in measured inputs can be expected, attributable to extreme experimental difficulty involved in solubility measurements in the ppb range or $K_{OW}$ and $K_{OC}$ measurements in the $10^6$ range. If the four high-molecular weight chlorinated compounds are excluded, the average deviation in $K_{OC}$ estimate from $X_{SOL}$ and mp is 0.27 log units which is a slight improvement over $K_{OC}$'s derived from $X_{SOL}$ alone.

The low molecular weight aliphatic chain compounds and cyclic BHC isomers do not show any systematic variations compared to aromatic compounds. No sorption data are available for longer chain (> $C_4$) aliphatics where entropy contributions to both sorption and melting (fusion) may deviate substantially from that associated with the "rigid" compounds treated herein.

Compounds with Polar Functional Groups. For polar compounds, good $K_{OC}$ estimates can be derived from either $K_{OW}$ (eq. 17) or $X_{SOL}$ and mp (eq. 13), whereas $X_{SOL}$ alone gives, in general, poor estimates of $K_{OC}$. For example, within the chloro-*s*-triazines, there is essentially no correlation between solubility and $K_{OC}$. In fact, the least soluble compound, simazine, is also the least sorbed. The solubilities of these compounds are heavily influenced by crystal energy, which is highly variable, as reflected in the 140°C range in melting points for these compounds of similar molecular weights. The average deviation between measured and solubility-derived log $K_{OC}$s is 0.74 log units. Inclusion of crystal energy (eq. 13) reduces this average deviation to 0.26 log units. The average deviation for $K_{OW}$-derived estimates was 0.31 log units.

This same trend is true for the other classes of polar compounds; irregular melting tends to destroy the correlation between sorption and solubility. In most instances, however, the inclusion of crystal energy considerably improves the $K_{OC}$ estimate. $K_{OW}$ gives good $K_{OC}$ estimates in most instances; the phenyl ureas present an interesting exception. The use of $K_{OW}$'s reported by Briggs (6) give $K_{OC}$'s consistently one order of magnitude less than the measured values. Therefore, $K_{OW}$ and $K_{OC}$ are highly correlated but are related by an equation substantially different from equations 16 or 17. It was first thought that this indicated either solute speciation changes or a non-hydrophobic sorption mechanism; however, recent $K_{OW}$ measurements for diuron and monuron (26) seem to point to measurement rather than chemistry as the source of the discrepancy.

## SUMMARY AND CONCLUSIONS

The approach used herein for estimation of equilibrium sorption behavior was a combination of thermodynamic theory and empirical correlation. Thermodynamic theory was used to suggest the mathematical form, and experimental data were used to confirm this "expected" behavior and/or empirically establish the constants in the equations.

For neutral hydrophobic solutes (generally water solubilities < $10^{-3}$ M), sorption isotherms in the low loading limit are linear, reversible, and can be characterized by a partition coefficient, $K_p$. These partition coefficients are highly correlated with the organic carbon content of sediments/soils; referencing sorption to organic carbon gives a partition coefficient to organic carbon, $K_{OC}$, which is highly sediment/soil independent.

$K_{OC}$s were estimated from commonly measured solute physical properties, namely octanol/water partitioning and solubility. The use of solubility with no crystal energy correction led to considerable error in $K_{OC}$ estimation for organic solids containing polar functional

groups (triazines and carbamates) and for anomalously high melting compounds (β BHC and anthracene). On the other hand, this corrected solubility equation apparently failed to extrapolate to high molecular weight chlorinated compounds (DDT, methoxychlor, hexachloro PCBs). Overall, for the vast majority of the available literature $K_{OC}$ data, estimates derived from octanol/water distribution coefficients or corrected solubilities were within the range of measurement variation, attributable to measurement error or reasonable differences in sediment/soil sorption.

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